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Intermolecular interactions in ternary liquid mixtures by ultrasonic velocity measurements

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Abstract : The densities, viscosities and ultrasonic velocities in ternary systems of 1-hexanol and 1-octanol in N,N-dimethylacetamide + ethanol mixtures have been measured at 303 K. From these data isentropic compressibilities, intermolecular free lengths, acoustic impedance, molar sound velocity, excess isentropic compressibilities, excess intermolecular free lengths, excess volumes, excess viscosities, excess acoustic impedances, and excess free energies of activation of viscous flow have been calculated These parameters are used to explain the nature of interaction between the component molecules of the mixtures. Moreover, theoretically evaluated values of ultrasonic velocities in these mixtures using Nomoto's and Van Dael and Vangeel's relations indicate superiority of the former relation over latter relation.

Keywords : Ternary liquid mixtures, acoustical parameters, molecular interaction

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1. Introduction

The study of molecular interactions in binary liquid mixtures has been extensively carried out from theoretical as well as experimental view points [1,2]. However, the study of the properties of ternary mixtures is scarce [3,4]. Multicomponent liquid mixtures are of great practical importance in many industrial processes, as they provide a wide choice of solutions with appropriate compositions and properties. Density, ρ, viscosity, η, ultrasonic velocity, u and derived parameters, such as isentropic compressibility, K_s, intermoleculer free length, L_f, acoustic impedance, Z, molar sound velocity, R_m, excess isentropic compressibility, K_s^E, excess intermolecular free length, L_f^E, excess acoustic impedance, Z^E, excess volume, V^E, excess viscosity, η^E and excess free energy of activation of viscous flow, G^{*E} provide a better insight into the intermolecular interactions, hence environment in the liquid mixtures. The aim of the present investigation is to study the molecular interactions in : (I) N,N-dimethylacetamide (DMA) + 1-hexanol + ethanol and (II) DMA + 1-octanol + ethanol ternary mixtures using the above mentioned properties at 303 K. Furthermore, no work has been reported in the literature for these ternary mixtures.

2. Experimental

The DMA, 1-hexanol, 1-octanol and ethanol used for the present work, were the same as in our previous studies [2,5,6], except that they were dried over 0.4 nm molecular sieves before use. The ternary mixtures of DMA + 1-hexanol + ethanol and DMA + 1-octanol + ethanol were prepared by weight and were kept in special airtight bottles. The weighings were done on Afcoset ER-120A electronic balance with a precision of ± 0.1 mg. The densities of pure liquids and their ternary mixtures were measured using a single stem pycnometer. The marks on the stem were calibrated with triple-distilled water. Viscosities were determined using Cannon-Ubbelohde viscometer. The accuracy of density measurements was ± 0.01 kg m^{-3} and the accuracy in viscosity was found to be $\pm 3\times10^{-6}$N m^{-2} s, respectively. Ultrasonic velocity was measured using a single-crystal variable-path interferometer at 3 MHz with an accuracy of

±0.05%. The temperature of test liquid mixtures was maintained at 303 ± 0.02 K in an electronically controlled thermostatic water bath.

3. Theory

The experimental values of density and ultrasonic velocity were used to calculate the isentropic compressibility K_s [7,8], intermolecular free length L_f [9,10], acoustic impedance Z [11] and molar sound velocity R_m [12] using the following relations :

$$K_s = u^{-2}\rho^{-1} \tag{1}$$

$$L_f = KK_s^{1/2} \tag{2}$$

$$Z = u\rho, \tag{3}$$

$$R_m = u^{1/3}V \tag{4}$$

where K is Jacobson's constant [9] and V is the molar volume of the mixture. The excess functions Y^E have been calculated using the relations :

$$Y^E = Y_{exp} - Y_{ideal}, \tag{5}$$

and $$Y_{ideal} = x_1Y_1 + x_2Y_2 + x_3Y_3$$

where Y denotes K_s, L_f, V, η, Z, respectively; x is the mole fraction (in case of isentropic compressibility, volume fraction ϕ instead of x is used); suffixes 1, 2 and 3 represent the mixture components. In ternary mixtures, the excess free energy of activation of viscous flow, G^{*E} is calculated using the relation :

$$G^{*E} = RT\left[\ln \eta V - (x_1 \ln \eta_1 V_1 + x_2 \ln \eta_2 V_2 + x_3 \ln \eta_3 V_3)\right]. \tag{6}$$

Ultrasonic velocity has been theoretically evaluated as a function of composition, using Nomoto's empirical relation [13] and Van Dael and Vangeel [14] ideal mixing relation The details of the derivations of these relations are given elsewhere [11,15].

4. Results and discussion

The experimental values of densities, viscosities and ultrasonic velocities and the derived parameters K_s, L_f, Z and R_m are presented in Table 1. It is evident that the values of K_s, L_f, R_m and η decrease while those of Z exhibit opposite trend as the mole fraction x_1 of DMA increases in the systems under study. The variation of u through the mixtures depends on the value of L_f. The observed increase in u and the corresponding decrease in L_f with composition for both the systems are in accordance with the view proposed by Eyring and Kincaid [16].

A qualitative interpretation of the behaviours of the above parameters with composition may be proposed. The molecules of alkanols (ethanol, 1-hexanol and 1-octanol) are

Table 1. Values of density (ρ), viscosity (η), ultrasonic velocity (u), isentropic compressibility (K_s), intermolecular free length (L_f), acoustic impedance (Z) and molar sound velocity (R_m) of (I) DMA + 1-hexanol + ethanol and (II) DMA + 1-octanol + ethanol ternary mixtures at 303 K.

Mole fraction		ρ	η	u	K_S	L_f	Z	R_m
x_1	x_2	(kg m^{-3})	(10^{-3} N m^{-2} s)	(m s^{-1})	(10^{-10} m^2 N^{-1})	(10^{-11} m)	(10^6 kg m^{-2} s^{-1})	[10^{-4} m^3 mol^{-1} (ms^{-1})$^{1/3}$]
				System I				
0.1131	0.5453	818.5	2.0925	1277.2	7.4897	5.6803	1.0454	1.0778
0.2229	0.4406	831.1	1.7147	1296.7	7.1560	5.5523	1.0777	1.0489
0.3289	0.3400	846.8	1.4530	1308.4	6.8982	5.4514	1.1080	1.0158
0.4304	0.2434	860.8	1.2498	1328.3	6.5847	5.3260	1.1434	0.9883
0.5301	0.1497	875.9	1.0903	1359.4	6.1780	5.1589	1.1907	0.9641
0.6255	0 0588	890 6	0.9574	1369.9	5.9833	5.0770	1.2200	0.9359
				System II				
0.1265	0.4856	819.8	2.7814	1303.5	7.1791	5.5612	1.0686	1.2276
0.2452	0.3835	837.1	2.1323	1318.7	6.8696	5.4400	1.1039	1.1582
0.3542	0.2894	848.7	1.7036	1326.7	6.6942	5.3701	1.1260	1.1001
0.4533	0.2019	861.0	1.3971	1335.7	6.5100	5.2957	1.1500	1.0446
0.5473	0.1214	885.9	1.1796	1351.1	6.1836	5.1613	1.1969	0.9828
0.6318	0.0476	893.1	0.9919	1369.5	5.9700	5.0714	1.2231	0.9451

associated in pure state through hydrogen bonding. Mixing of DMA with alkanols would release the dipoles of alkanols due to breaking of hydrogen bonds. As a result, the free dipoles of alkanols interact with DMA molecules forming strong hydrogen bonds [2] leading to contraction in volume, hence, reduction in compressibility and free length of the mixtures. However, the strength of hydrogen bond formed between DMA and alkanol molecules should follow the order : ethanol > 1-hexanol > 1-octanol. This is due to the fact that molecular size of ethanol (molar volume = 5.8770×10^{-5} m^3 mol^{-1}) is much smaller than those of 1-hexanol (molar volume = 12.6520×10^{-5} m^3 mol^{-1}) and 1-octanol (molar volume = 15.9320×10^{-5} m^3 mol^{-1}) which would allow a closer approach, hence, stronger association between DMA and ethanol molecules than between DMA and 1-hexanol/1-octanol molecules. A similar explanation for the decrease in compressibility with composition for liquid mixtures has also been suggested by Fort and Moore [17].

Table 1 shows that there is a continuous decrease in viscosity η as the amount of 1-hexanol in system I and that of 1-octanol in system II decreases. Thus, it is concluded that the magnitude of η depends mainly on the availability of bulky or less mobile entities of 1-hexanol and 1-octanol components in their respective mixtures. Such qualitative interpretation of η is supported by the view [18,19] that viscosity of a system is determined mainly by the bulky or less mobile entities of the system. An increase in the value of Z and decrease in R_m with mole fraction of DMA (Table 1) for both the systems are in good agreement with the requirements given in eqs. (3) and (4). This is because ρ and u increase while V decreases (Table 1) and the effect of V seems to dominate over that of u in deciding the trend of R_m.

The calculated values of excess functions, using the eqs. (5) and (6), are listed in Table 2. It is evident that K_s^E and L_f^E are negative for all values of concentration, both showing minimum at 0.5301 mole fraction of DMA in system I and at 0.6318 mole fraction in system II. The negative excess compressibility and free length are attributed to the presence of molecular interactions, possibly, through hydrogen bonding between unlike molecules. Ramamoorthy and Sastry [20] and Palaniappan *et al* [21] pointed out that negative values of excess intermolecular free length L_f^E indicates that sound wave covers longer distance due to decrease in intermolecular free length as a result of hydrogen bond formation between unlike molecules.

The excess volumes V^E are negative for all the concentrations for the system I, which further supports the existence of interaction between unlike molecules. For the system II, V^E has more negative values and few positive values.

Table 2. Values of excess isentropic compressibility (K_s^E), excess intermolecular free length (L_f^E), excess volume (V^E), excess viscosity (η^E), excess acoustic impedance (Z^E) and excess free energy of activation of viscous flow (G^{*E}) of (I) DMA + 1-hexanol + ethanol and (II) DMA + 1-octanol + ethanol ternary mixtures at 303 K

Mole fraction		K_s^E	L_f^E	V^E	η^E	Z^E	G^{*E}
x_1	x_2	(10^{-11} m^2 N^{-1})	(10^{-12} m)	(10^{-7} m^3 mol^{-1})	(10^{-3} N m^{-2} s)	(10^4 kg m^{-2} s^{-1})	(J mol^{-1})
				System I			
0.1131	0.5453	-6.0156	-1.9675	-3.0368	-0.4739	2.5987	162.76
0.2229	0.4406	-6.6509	-2.1386	-1.7428	-0.5337	2.4049	52.73
0.3289	0.3400	-6.6082	-2.0731	-3.5005	-0.4898	2.1192	1.07
0.4304	0.2434	-7.2411	-2.2996	2.9678	-0.3995	2.4920	-24.01
0.5301	0.1497	-8.8217	-2.9521	-2.9041	-0.2742	4.0972	-27.94
0.6255	0.0588	-8.4201	-2.8078	-2.1077	-0.1310	4.0549	-26.48
				System II			
0.1265	0.4856	-7.0187	-2.3005	3.9103	-0.8724	2.7595	591.53
0.2452	0.3835	-7.5364	-2.4552	-2.3120	-0.9445	2.9344	408.23
0.3542	0.2894	-6.9335	-2.1869	-0.5712	-0.8414	2.0712	300.62
0.4533	0.2019	-6.6917	-2.0727	0.4158	-0.6537	1.7233	217.83
0.5473	0.1214	-7.9039	-2.5763	-10.8610	-0.4161	3.7516	134.64
0.6318	0.0476	-8.2381	-2.7347	-3.8692	-0.1869	4.0030	53.91

Similar behaviour of V^E with concertration has also been reported by Kannappan and Palani [10] and Kumar and Naidu [22] in ternary liquid mixtures. The observed excess viscosities η^E are negative for both the systems over the concentration range investigated (Table 2). Negative η^E deviations from rectilinear dependence on mole fraction may occur where dispersion forces are dominant, particularly, for the systems having different molecular size [17,19] as in the present systems. It should be noted that the system II (DMA + 1-octanol + ethanol) exhibits more pronounced negative η^E than the system I (DMA + 1-hexanol + ethanol), which is attributd to the greater differences in the sizes of the component molecules in the former system than in the latter system, supporting the view proposed by others [17,19].

Both the ternary systems exhibit positive values of excess acoustic impedance Z^E (Table 2) at all concentrations of the mixtures. The expected positive deviations in Z^E, where $Z = u\rho$, and opposite trend in the behaviour of K_s^E, where $K_s = 1/u^2\rho$, over the concentration range studied again reinforce our view that significant interactions are present between unlike molecules in the systems. The excess free energies of activation of viscous flow G^{*E} change from positive to negative values in system I and become large positive in system II. According to Reed and Taylor [23], Meyer *et al* [24] and Oswal and Rathnam [25], the positive deviation in G^{*E} may be attributed to specific interactions, hydrogen bonding and dipole-dipole, where as the negative deviations may be ascribed to dispersion forces in the system. Recently, Oswal and Desai [26] attributed the increasing positive values of G^{*E} to the large size and cohesive energy difference between the unlike components of the mixture, as in the present systems.

The values of ultrasonic velocities in the systems under study were computed theoretically using Nomoto and ideal mixing relations. The calculated values of ultrasonic velocity together with the experimental velocities and average percentage deviations in the calculated values compared with the experimental values are listed in Table 3. From Table 3, it is evident that the ultrasonic velocities calculated using Nomoto's relation deviate from the experimental values in the range 1.17 to 8.74 percent in the system I and 2.03 to 5.04 percent in the system II, while in case of ideal mixing relation the corresponding deviations in the two systems are in the range 6.99 to 17.60 percent and 11.50 to 20.97 percent. These results indicate that, for the ternary mixtures studied, Nomoto's relation is best suited for the evaluation of ultrasonic velocity than ideal mixing relation.

5. Conclusion

The trends in the variation of parameters derived from ultrasonic velocity and the sign and magnitude of the excess functions suggest the presence of molecular interaction in the

Table 3. Theoretical ultrasonic velocities calculated using Nomoto's relation and ideal mixing relation along with experimental values and percentage error as compared with the experimental values for (I) DMA + 1-hexanol + ethanol and (II) DMA + 1-octanol + ethanol ternary mixtures at 303 K.

Mole fraction		u_{Exp}	u_{Nomoto}	$u_{Ideal\ mixing\ relation}$	Percentage error	
x_1	x_2	(m s^{-1})	(m s^{-1})	(m s^{-1})	Nomoto	Ideal mixing relation
			System I			
0.1131	0.5453	1277.2	1292.2	1187.9	1.17	6.99
0.2229	0.4406	1296.7	1282.2	1174.2	1.12	9.45
0.3289	0.3400	1308.4	1273.2	1161.6	2.69	11.22
0 4304	0.2434	1328.3	1264.9	1149 9	4.77	13 43
0.5301	0.1497	1359 4	1257.3	1139.2	7.51	16.20
0.6255	0.0588	1369.9	1250.2	1128.8	8.74	17.60
			System II			
0.1265	0.4856	1303.5	1330.0	1153 6	2 03	11.50
0.2452	0.3835	1318.7	1321.2	1131.5	0.19	14.19
0.3542	0.2894	1326.7	1314.4	1114.5	0.93	16.00
0.4533	0.2019	1335.7	1308.6	1100.6	2.03	17.60
0.5473	0.1214	1351.1	1304.3	1090.5	3.47	19.29
0.6318	0.0476	1369.5	1300.5	1042 3	5.04	20.97

present ternary liquid mixtures. It may be concluded (qualitatively) that the interaction between unlike components is mainly due to hydrogen bonding through highly polar oxygen atom of dimethylacetamide and hydrogen atom of alkanols. Moreover, dispersion forces also seem to exist between the components of the mixtures. Nomoto's relation is found to fit the data better than ideal mixing relation.

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